

Calibration of Auger and X-ray photoelectron spectrometers for valid analytical measurements

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Introduction

Auger Electron Spectroscopy (AES) and X-Ray Photoelectron Spectroscopy (XPS) are the most popular techniques for identifying elements and chemical states present in the outermost 5 nm at the surface of a solid sample.¹⁻³ This typically represents the first 10–20 atomic layers. Combined with ion-beam sputtering,¹ chemical depth profiles can be constructed to depths about 1 μm below this surface and therefore these spectroscopies are being used increasingly in microelectronics,¹ chemicals,^{1,2} biomaterials,³ corrosion¹ and adhesion¹ research. In the 1990s, production testing and fault diagnosis applications have emerged to be increasingly important, for instance in semiconductor fabrication and the production of magnetic data storage media.

AES and XPS are “intrinsically quantitative” methods. In principle, with good instrumental design, one can obtain a percentage analysis of surface composition. Modern instrument design is not just good—it is excellent, with high-throughput spectrometers commercially available from a number of manufacturers. There is a relentless pressure from the market to develop instruments with ever greater throughput and hence greater count detection rate. Impressive innovation in electron-optics and detection electronics has led to instruments capable of performing analyses in a very short time compared with the instruments available in the early 1980s. However, spectrometer calibration has been made a more subtle task by these developments. At the simplest level, we have these two axes of the output spectrum to calibrate;

- The abscissa axis, representing electron energy (typically Binding Energy for XPS spectra and Kinetic Energy for AES spectra) plotted in units of electron-volts.

- The ordinate axis, representing the intensity of X-ray photoelectron or Auger emission from the surface.

Calibrating the energy scale

An accurate Binding Energy scale is particularly important in XPS. Oxidation states (and hence the compounds present at the surface) are identified by the small energy shifts their peaks show with respect to the energy of the corresponding peaks in the spectrum of the pure element. This is analogous to the chemical shifts one can measure from NMR spectra for example. An error of less than 0.5 eV in the Binding Energy scale can lead to *qualitative* errors; misinterpretation of the stoichiometry of what is present.

Energy calibration has recently been the focus for the development of documentary standards, under ISO TC/201 Committee on Surface Chemical Analysis.⁴ One of the first fruits seems likely to be an ISO Standard for Energy Calibration of X-Ray Photoelectron Spectrometers, currently under consideration at the draft stage. Typically the energy correction needed is small and linear with binding energy, although there are some important subtleties associated with the choice of interval between calibrations required to maintain the energy scale within specification. Easy-to-use methods of peak-location have also been proposed,⁵ which make calibration of the energy scale simpler and quicker.

Calibrating the intensity scale

Calibrating the intensity scale—the ordinate axis of the spectrum—is considerably more difficult than calibration

of the energy scale. First, there are potential causes of non-linearity of the intensity scale.⁶ An example is the “dead-time” interval after electron detection, during which the detector may be insensitive to further signal electrons. The higher the count rate, the greater the proportion of electrons missed, leading to a weakly non-linear intensity scale.

In most instruments⁷ only a small correction is required to remove this non-linearity. In the remainder of this article we will instead be concerned with the much stronger variations of the intensity scale of an instrument as the energy is scanned. A typical spectrometer will have a varying sensitivity with energy. Unfortunately, this differs from one model of spectrometer to the next, often from one individual instrument to the next. The physical causes for this variation in response have been set out previously in detail.^{8,9} Here we compare with how the same problem has been addressed in another field of spectroscopy, and arrive at a rather different solution within the very special constraints of AES and XPS.

Comparison with IR compensation

The major remaining obstacle to rapid, quantitative analysis by AES and XPS becomes clear when one compares an electron spectrometer with a device which has a much more mature history—the conventional continuous-wave infrared (IR) spectrometer. The earliest IR spectrometers consisted of simply a source, a sample, a monochromator and a detector, which allowed absorbance to be plotted. Since the 1940s, however, commercial IR spectrometers have been of the familiar “dual beam” or compensating type, shown schematically in Figure 1. This dual beam design helps eliminate mis-

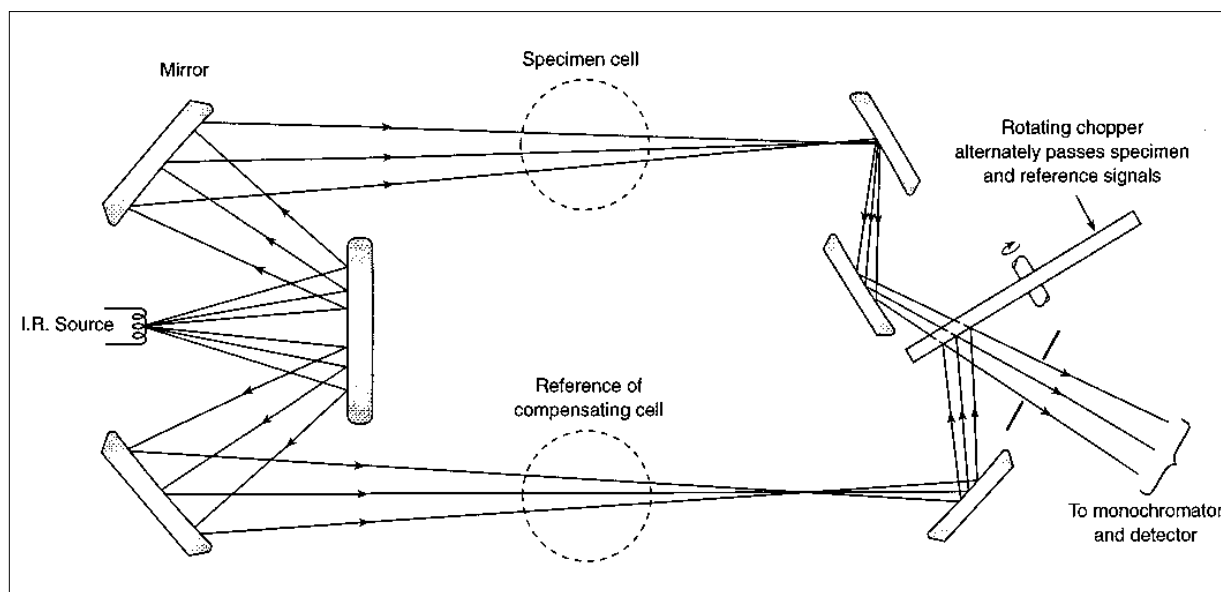


Figure 1. Schematic diagram showing the operation of "dual-beam" compensation in a continuous-wave IR spectrometer.

leading transmission features in the spectrum by detecting the difference in intensity between a beam passing through the sample and a reference beam. Intensity variations due to atmospheric absorption, emission characteristics of the source, or mirror reflectivity as a function of wavelength are common to both paths, and therefore largely eliminated. For analytes dissolved in a solvent, a sample of pure solvent can be placed in the path of the compensating beam and the spectrum of the solvent is thereby effectively removed from the spectrum recorded. This "dual beam" approach is clearly an excellent paradigm to apply to the design of any kind of spectrometer, cost and other practicalities permitting.

Figure 2 shows, schematically, the electron optical column of a typical commercial AES/XPS spectrometer. Despite the fact that this instrument represents about 50 times the capital investment of an IR spectrometer, it is nevertheless an uncompensated, single-beam instrument. No commercial electron spectrometer uses dual beam compensation. Although possibly feasible in principle, two lenses and two analysers would be needed, essentially doubling the cost of the instrument. Alternative arrangements based on rapidly switching between sample and reference material followed by phase-sensitive detection are equally unattractive. Nevertheless, the electron spectrometer is prone to just as many spurious transmission effects as the IR spectrometer. There are no solvent attenuation problems of course, since the entire electron trajectory is maintained at Ultra High Vacuum, but the analyser design, detector type, slit geometry and lens

optics all introduce transmission variations as a function of electron energy. Different limits come into play over different energy ranges, largely as a result of excellent design innovations during the evolution of these instruments in the last two decades to optimise count-rate. These factors do not add spurious peaks to the AES or XPS spectrum (as is potentially the case in IR spectroscopy) so qualitative analyses of surface composition have been performed reliably for years. However, *quantitative* analysis is made very diffi-

cult and time-consuming by these transmission artefacts; different models of spectrometer (and even different spectra from the *same* spectrometer recorded over a period of time as the detector ages) show significantly different transmission as a function of energy. The right-hand panel of Figure 3(a) shows XPS spectra of an air-exposed magnesium surface recorded using two different commercial spectrometers. To obtain a chemical analysis of the oxide formed at this surface one must take the intensities of oxygen O 1s and

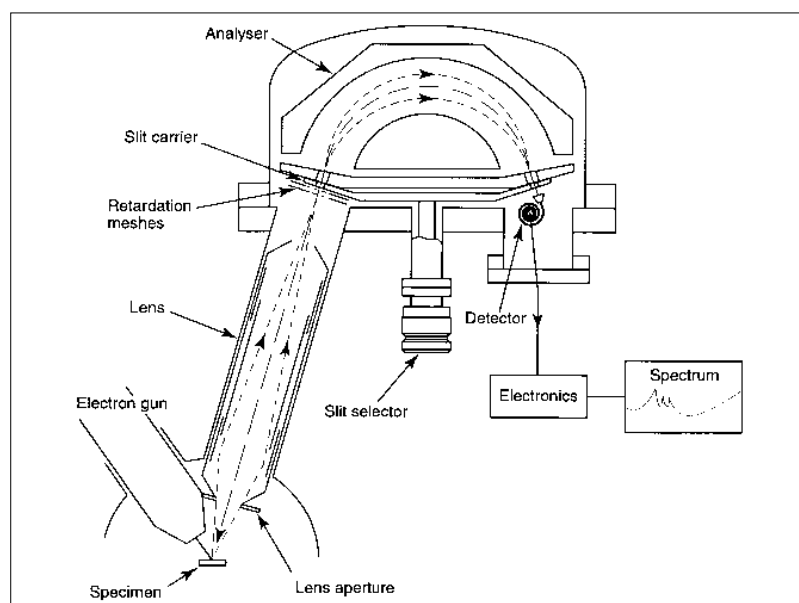


Figure 2. The electron-optics of a typical XPS spectrometer consist of a transfer lens, analyser and detector. Although each can affect the response of the instrument, the design is nevertheless a single-beam uncompensated type, in contrast to the IR spectrometer shown in Figure 1.

magnesium peaks, weight them with sensitivity factors published by the instrument manufacturer, and then use their ratios to calculate the percentage composition or stoichiometry. These sensitivity factors represent, in part, the transmission properties of that model of spectrometer which in the “dual-beam” IR spectrometer is automatically compensated for.

What is worse, the tables of “sensitivity-factors” published by AES/XPS spectrometer manufacturers are often incomplete. Instrument response can vary from spectrometer to spectrometer within the same model range, and the response for an individual instrument can change with the spectrometer settings or as the detector ages. Therefore, even the published sensitivity factors are rather approximate. This leads to an unnecessary degradation of the accuracy of one’s quantitative analysis, so that an error of a factor of two can occur.⁸

Solutions

Those analysts dealing with a very small range of elements, but with high analytical throughput (for example, in semiconductor fabrication) can afford the cost of developing special reference materials which allow sensitivity factors to be measured accurately for their own instrument and operating conditions. Most of us, however, have to deal with a wide range of samples in standard-less analyses.

The solution is an “off-line” compensation method.⁹ By recording spectra for easily-prepared surfaces such as pure copper, silver and gold one can determine the response function of the spectrometer by dividing them with known true spectra acquired on calibrated, standard instruments, such as the Metrology Spectrometer II¹⁰ developed at NPL. The background of inelastically scattered electrons (which is usually a nuisance in AES and XPS) is a real advantage here because it allows the response of the instrument over the entire energy range to be measured using just two or three reference samples. This compensation process can be performed for AES or XPS. Examples of the response functions of two instruments of each type are shown in Figure 3(b). Using this known instrument response, one can calculate sensitivity factors for one’s instrument from tabulated values which are essentially atomic standards rather than compilations valid only for particular instruments. Alternatively, one can simply divide all subsequent spectra which one acquires by the response function, giving true spectra which are genuinely comparable with those from

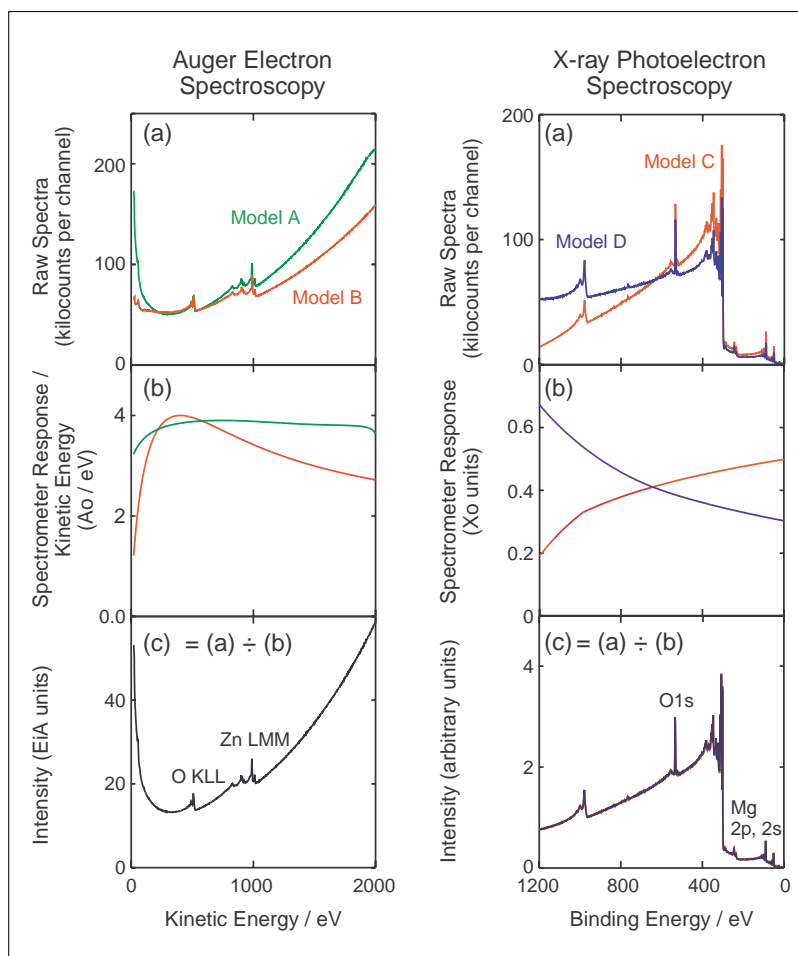


Figure 3. This schematic tableau shows how spectra from different calibrated instruments can be corrected to allow quantitative analysis in AES and XPS. (a) shows raw spectra from two AES and two XPS instruments, each pair of instruments from different manufacturers. The AES spectra represent a single sample of ZnO, and the XPS spectra a partially air-oxidised magnesium surface. Each instrument has previously been calibrated using the method described in the text, giving response functions shown in (b). Dividing the raw spectra by the response function gives AES and XPS spectra shown in (c), which are genuinely comparable with those from any other calibrated instrument. Note that, unlike the original raw spectra shown in (a), the corrected spectra in (c) show the correct intensity ratios of the labelled metal and oxygen peaks, allowing quantification of oxide stoichiometry in a way which is impossible to do reliably on an uncalibrated instrument.

any other instrument, as shown in Figure 3(c). What is more, if one is able to measure the primary beam intensity (this is fairly straightforward in AES) the corrected spectra will be in SI units; this is true *calibration* not just compensation, a genuine improvement over the analogous IR instrument discussed above. One can then trace the efficiency of an instrument over time, or compare the performance of instruments, in a way hitherto impossible.

Although we have described the calibration as a simple division operation in principle, there are a number of subtleties in this calibration process, not least the acquisition of the “true” spectra themselves. Over the last decade,

work at NPL has developed from acquiring these standard spectra using a specially constructed spectrometer, to conducting interlaboratory comparisons to verify the calibration method,¹¹ finally resulting in a “user friendly” software package¹² allowing the analyst to perform the calibration (as shown in Figure 3) as quickly and easily as possible.¹³ For those interested in the details of the calibration scheme, a full description of its mathematical structure has been published.⁹

Bear in mind that changing the slits or pass-energy of the analyser can change the relative intensities of low and high energy peaks by a factor of two, though even larger differences

may occur between instruments of the same model operated under apparently identical settings in different laboratories. Interlaboratory comparisons have shown that each instrument needs a separate and regular calibration, and that such a procedure can reduce intensity variations from a scatter of 700% over the energy range 200–1400 eV to an average of 2–4%.

A mathematical function for instrument response

The response of the spectrometer at any kinetic energy, E , is the product of a number of terms, such as the response of the channel electron multiplier or channel plate detector (see Table 1).

The detector efficiency is an important factor in determining instrument response in AES at constant retard ratio (one of the most useful operating modes). This detector function is reasonably simple and is described by the complex secondary electron cascade within the detector itself. We might hope that the response of the entire spectrometer could be approximated by such physically derived functions, however, modern spectrometers are seldom so simple. Excellent design has led to much improved count-rates, generally by optimising the components of the spectrometer and detector to the point where more than one of them determines the response function over the energy range of a typical spectrum. As the energy, E , is scanned, the transition between two different limiting factors leads, in principle, to a rapid change in the first derivative of the instrument response function $Q(E)$. For example, at low kinetic energies the transmission of the optics may be limited by one field-stop, slit or iris, whilst at higher energies it is limited by another. The transition between the two regimes can be modelled physically, but is unique to each spectrometer, and given the wide range of instrument designs currently available, needs a general solution. Fitting to a polynomial is equally unattractive, because of the

large number of terms one would need to achieve the accuracy required and rapidly unphysical asymptotic behaviour which makes a polynomial calibration difficult to use near its energy limits. We chose instead a rational function of nine parameters.

$$Q(E) = \frac{a_0 + a_1\varepsilon + a_2\varepsilon^2 + a_3\varepsilon^3 + a_4\varepsilon^4}{1 + b_1\varepsilon + b_2\varepsilon^2 + b_3\varepsilon^3 + b_4\varepsilon^4}$$

where $\varepsilon = (E - 1000 \text{ eV})/1000 \text{ eV}$.

The calibration therefore provides values for the nine coefficients a_0 to b_4 , which then allow one to calculate the response function easily, but with sufficient flexibility to model the most pathological response functions to within 1% over the entire interval of calibration. Typical fitted response functions for AES and XPS are shown in Figure 3(b). The rational function has advantages over polynomial approximation in its ability to handle rapid changes in slope while retaining smooth behaviour between such features, and in remaining well-behaved right up to the end of the interval over which the calibration is being performed. The fit here is non-linear, and as the fitting algorithm must be chosen with care, we begin by performing a fit to a nine parameter polynomial and then apply a Pade approximation¹⁴ to obtain good starting values for an iterative fit to find the nine rational function parameters.

Conclusions

In this article we have outlined the basic calibration of Auger and X-ray photoelectron spectrometers. The appearance of these compensation and calibration methods is a significant landmark in the increasing maturity of Auger and X-ray photoelectron spectroscopy as quantitative analytical methods. These are vital for researchers and analysts conducting general quantitative work, and are carefully designed to assist those working within laboratory quality management schemes such as those based on ISO 9000 and especially ISO Guide 25.

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Table 1. Main factors influencing instrument response.

| Auger electron spectroscopy | X-Ray photoelectron spectroscopy |
|-----------------------------|----------------------------------|
| — Age of detector | — Pass energy |
| — Retard ratio | — Slits and apertures |
| — Stray magnetic fields | — Analysis area |